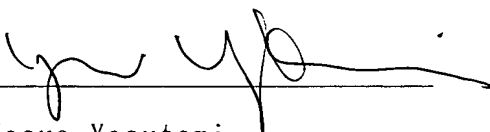


VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome,
Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am
conversant with the Japanese and English languages and that I am the
translator of the documents attached and certify that to the best of
my knowledge and belief the following is a true and correct English
translation of the Japanese Patent Application No. Hei 10-147809
in the name of KANEKA CORPORATION.

Dated this *6th* day of *August*, 2004



Yasuo Yasutomi

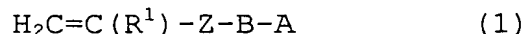
[Document Name] Patent Application
[Filing Number] KEN-3483
[Filing Date] May 28, Heisei 10
[To] Commissioner, Patent Office
[IPC] C08F 20/18
[Title of the Invention] POLYMER AND METHOD OF PRODUCING POLYMER
[Number of Claims] 29
[Inventor]
[Address or Residence] c/o Kobe Research Laboratories Research
Institute of Kaneka Corporation
2-80, Yoshidacho 1-chome, Hyogo-ku,
Kobe-shi, HYOGO
[Name] NAKAGAWA Yoshiki
[Inventor]
[Address or Residence] c/o Kobe Research Laboratories Research
Institute of Kaneka Corporation
2-80, Yoshidacho 1-chome, Hyogo-ku,
Kobe-shi, HYOGO
[Name] KIMURA Katsuhiko
[Applicant]
[Identification Number] 000000941
[Name] KANEKA CORPORATION
[Representative] FURUTA Takeshi
[Indication of Fee]
[Number of Deposit Ledger] 005027
[The Amount of Payment] 21,000 yen
[List of Attached Documents]
[Document Name] Description 1
[Document Name] Abstract 1
[Necessity of Proof] Needed

[Document Name] Description

[Title of the Invention] POLYMER AND METHOD OF PRODUCING
POLYMER

[Scope of Claims for Patent]

- 5 [Claim 1] A block copolymer which is produced by adding a
block copolymer (I) represented by the general formula 1:



- (wherein R^1 represents a hydrogen atom or a hydrocarbon group
containing 1 to 20 carbon atoms, Z represents a divalent organic
10 group, and A and B each represents a polymer block) to a living
cationic polymerization system.

[Claim 2] The block copolymer according to Claim 1, wherein,
in the general formula 1, R^1 is a hydrogen atom.

- [Claim 3] The polymer according to Claim 1 and 2, wherein
15 the polymer blocks A and B in the block copolymer (I) are
respectively selected from the group consisting of a styrenic
polymer, a (meth)acrylic polymer, and an acrylonitrile polymer.

- [Claim 4] The polymer according to Claims 1 to 3, wherein
the polymer block A is a styrenic polymer, and the polymer block
20 B is an acrylic polymer in the block copolymer (I).

[Claim 5] The polymer according to Claims 1 to 3, wherein
the polymer block A is a methacrylic polymer, and the polymer
block B is an acrylic polymer in the block copolymer (I).

- [Claim 6] The polymer according to Claims 1 to 3, wherein
25 the polymer block A is a methacrylic polymer, and the polymer
block B is a styrenic polymer in the block copolymer (I).

[Claim 7] The polymer according to Claims 1 to 6, wherein
the block copolymer (I) has the number average molecular weight
of 500 to 100000.

- 30 [Claim 8] The polymer according to Claims 1 to 7, wherein
the polymer (I) has the ratio between the weight average
molecular weight (M_w) and the number average molecular weight
(M_n) (M_w/M_n) as determined by gel permeation chromatography of
not more than 1.8.

- 35 [Claim 9] The polymer according to Claims 1 to 8, wherein

the block copolymer (I) is produced by controlled radical polymerization.

[Claim 10] The polymer according to Claim 9, wherein the block copolymer (I) comprises a vinyl polymer produced by
 5 polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst.

[Claim 11] The polymer according to Claim 10, wherein the
 10 metal complex to serve as a catalyst for producing the block copolymer (I) is a copper, nickel, ruthenium or iron complex.

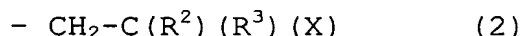
[Claim 12] The polymer according to Claim 11, wherein the metal complex to serve as a catalyst for producing the block copolymer (I) is a copper complex.

[Claim 13] The polymer according to Claim 9, wherein the block
 15 copolymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using a chain transfer agent.

[Claim 14] The polymer according to Claim 10, wherein the
 20 block copolymer (I) is produced by using an alkenyl-containing organic halide or a sulfonyl halide as an initiator.

[Claim 15] The polymer according to Claim 14, wherein the block copolymer (I) is produced by using an allyl halide as an initiator.

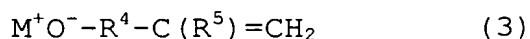
[Claim 16] The polymer according to Claims 1 to 15, wherein
 25 the block copolymer (I) is produced by converting a halogen group of a vinyl polymer having a terminal structure represented by the general formula 2:



(wherein R^2 and R^3 may be the same or different and each
 30 represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.

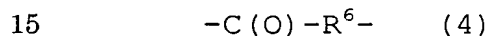
[Claim 17] The polymer according to Claim 16, wherein the
 35 block copolymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula

3:



(wherein R^4 represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R^5 represents hydrogen, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M^+ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula 2.

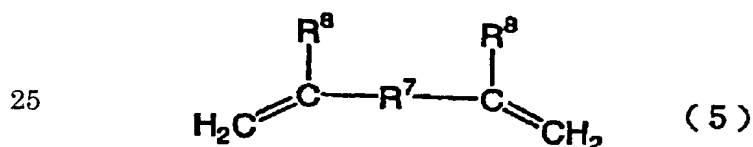
[Claim 18] The production method according to Claim 17, wherein, in the general formula 3, R^4 of the alkenyl-containing oxy anion is a divalent organic group represented by the following general formula 4:



(wherein R^6 represents a direct bond, or a divalent organic group containing 1 to 19 carbon atoms which may optionally contain one or more ether bonds or ester bonds).

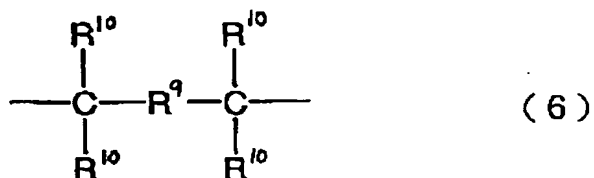
[Claim 19] The polymer according to Claims 1 to 14, wherein the block copolymer (I) is produced by adding a compound represented by the general formula 5:

[Chemical 1]



(wherein R^7 represents an alkyl group containing 1 to 20 carbon atoms, or a group having a structure represented by the general formula 6:

[Chemical 2]

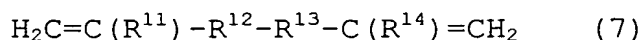


(wherein R^9 represents an oxygen atom, nitrogen atom or

organic group containing 1 to 20 carbon atoms; R^{10} may be the same or different and represents a hydrogen atom or a methyl group) and R^8 represents a hydrogen atom or a methyl group} during or after completion of living radical polymerization.

5 [Claim 20] The polymer according to Claims 1 to 14, wherein the block copolymer (I) is produced by adding a compound having both an alkenyl group with high radical polymerizability and an alkenyl group with low radical polymerizability during or after completion of the living radical polymerization.

10 [Claim 21] The polymer according to Claim 20, wherein the compound having both an alkenyl group with high radical polymerizability and an alkenyl group with low radical polymerizability is represented by the general formula 7:



15 (wherein R^{11} and R^{14} represent hydrogen or a methyl group, R^{12} represents $-C(O)O-$ (ester group), or an ortho-, meta-, para-phenylene group, and R^{13} represents a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may optionally contain one or more ether bonds).

20 [Claim 22] The polymer according to Claims 1 to 21, wherein a polymer chain produced by living cationic polymerization has a glass transition point not higher than 25°C.

[Claim 23] The polymer according to Claim 22, wherein the block copolymer (I) is added to a living cationic polymerization system of isobutylene.

[Claim 24] The polymer according to Claims 1 to 23, wherein the living cationic polymerization is started from a di- or more functional initiator.

30 [Claim 25] The polymer according to Claims 1 to 24, wherein the living cationic polymerization is carried out in a solvent without containing methylene chloride.

[Claim 26] The polymer according to Claim 25, wherein the living cationic polymerization is carried out in a solvent containing toluene.

35 [Claim 27] The polymer according to Claims 1 to 26 which has

a structure of A-B-C-B-A (wherein A and B are the same as defined above, and C is an isobutylene polymer).

[Claim 28] A thermoplastic elastomer which comprises, as the main component thereof, the polymer according to Claims 1 to 5 27.

[Claim 29] An impact resistance improving agent which comprises, as the main component thereof, the polymer according to Claims 1 to 27.

[Detailed Description of the Invention]

10 [0001]

[Technical Field of the Invention]

The present invention relates to a method for producing a block copolymer containing three or more polymer blocks which comprises adding an alkenyl-terminated block copolymer to a 15 living cationic polymerization system, the polymer, and its use.

[0002]

[Prior Art]

Block copolymers composed of different polymer block 20 species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block copolymers using them. When cationic polymerization is 25 employed, however, it is difficult to control the polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the cationic polymerization is inhibited from undergoing 30 isomerization, chain transfer reaction or termination reaction have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using a combination of hydrogen iodide and iodine as an initiator. 35 However, the polymerization using such initiator has various

problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, and the initiator is unstable and difficult to handle.

5 [0003]

On the other hand, Kennedy et al. (Japanese Kokai Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as isobutylene, using an organic carboxylic acid or an ester, or
10 an ether as an initiator in combination with a Lewis acid, showed that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has succeeded in obtaining block copolymers by successive monomer
15 addition with additional use of an amine. In this modification, isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in an mixed solvent composed of methylene chloride and hexane. However, such halogenated hydrocarbons containing 1 or 2 carbon atoms have
20 problems; for instance, they are difficult to handle, and require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also possible in a halogen-free solvent such as toluene, very fine
25 adjustment is required, depending on the monomer, for the monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.

[0004]

30 Meanwhile, as for a block copolymer containing three or more species of blocks, it is possible to adjust wider range of the physical property than a polymer comprising two species of blocks by adjusting the species or molecular weight of the block copolymer. However, it is more difficult to produce such
35 block copolymer than to produce a polymer comprising two species

because of such reasons as mentioned above.

[0005]

[Subject which the Invention is to Solve]

The present invention has for its object to provide a
5 method for easily producing a block copolymer, which contains
three or more species of polymer blocks, comprising any of
various polymers and a cationic polymerization polymer, without
requiring optimization of polymerization conditions which is
difficult to achieve.

10 [0006]

[Means for Solving the Problems]

The present invention relates to a block copolymer which
is produced by adding a block copolymer (I) represented by the
general formula 1:

15
$$\text{H}_2\text{C}=\text{C}(\text{R}^1)-\text{Z}-\text{B}-\text{A} \quad (1)$$

(wherein R^1 represents a hydrogen atom or a hydrocarbon group
containing 1 to 20 carbon atoms, Z represents a divalent organic
group, and A and B each represents a polymer block) to a living
cationic polymerization system.

20 [0007]

The block copolymer (I) is preferably polymerized by
controlled radical polymerization, and more preferably by the
living radical polymerization. The terminal group is
introduced by the initiator and various functional group
25 conversions. The block copolymer (I) also has a characteristic
for having a narrow molecular weight distribution.

The living cationic polymerization for adding the block
copolymer (I) is not particularly restricted, but preferred is
the atom transfer radical polymerization.

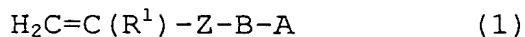
30 [0008]

The block copolymer of the present invention is useful
as a thermoplastic elastomer or an impact resistance improving
agent.

[0009]

35 [Embodiment of the Invention]

The present invention relates to a block copolymer which is produced by adding a block copolymer (I) represented by the general formula 1:



- 5 (wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, Z represents a divalent organic group, and A and B each represents a polymer block) to a living cationic polymerization system.

[0010]

- 10 In the general formula 1, R^1 is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:

- $(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
 - $\text{CH}(\text{CH}_2\text{CH}_3)_2$, - $\text{C}(\text{CH}_3)_2-(\text{CH}_2)_n-\text{CH}_3$, - $\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
 15 - C_6H_5 , - $\text{C}_6\text{H}_5(\text{CH}_3)$, - $\text{C}_6\text{H}_5(\text{CH}_3)_2$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)$,
 - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)_2$

(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

- 20 [0011]

Z group in the block copolymer (I) is a divalent organic group, and is not particularly restricted. It is defined by various introduction methods described in this description.
 <Monomer >

- 25 The polymer blocks A and B in the block copolymer (I) of the present invention are not restricted, but preferably are vinyl polymers. The vinyl monomer constituting the polymer is not particularly restricted and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid,
 30 methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl
 35 (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl

(meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate,

5 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl

10 (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate,

15 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, α -methylstyrene, chlorostyrene, styrenesulfonic acid and

20 salts thereof; fluorine-containing vinyl monomers such as perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and

25 dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and

30 cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate;

35 alkenes such as ethylene and propylene; conjugated dienes such

as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products. Additionally, the various polymer blocks may be copolymers of some monomers.

[0012]

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the block copolymer (I) of the present invention is not particularly restricted but is preferably not more than 1.8, more preferably not more than 1.6, and most preferably not more than 1.3.

The number average molecular weight of the block copolymer (I) of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably within the range of 3,000 to 40,000.

The glass transition point of the block copolymer (I) is preferably not lower than 25°C in view of physical properties of the product block copolymer and the like.

<Method of producing the block copolymer (I)>

The method of producing the block copolymer (I) is not particularly restricted but said polymer is preferably produced by controlled radical polymerization. As the controlled radical polymerization, there may be mentioned polymerization which comprises using a chain transfer agent, or living radical polymerization which has been recently developed. The latter is preferable from the polymerization controllability point of view.

[0013]

The method of introducing an alkenyl group to the terminus of the block copolymer (I) is not particularly restricted, but there may be mentioned a method comprising carrying out living radical polymerization using an alkenyl-containing initiator,

a production method comprising converting a halogen group of a vinyl polymer having the terminal structure represented by the general formula 2:



5 (wherein R^2 and R^3 may be the same or different and each represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) which is produced by a polymerization using a chain transfer agent, living radical polymerization, or the
10 like to an alkenyl-containing substituent, and a method comprising adding a group which is, in the living radical polymerization system, capable of reacting with the growing terminus, and an alkenyl-containing compound.

[0014]

15 Herein, the term "a group bound to a vinyl group of a vinyl monomer" as used in the present invention is described.

The vinyl monomer of the present invention is a compound represented by $CH_2=C(R^2)(R^3)$ (wherein R^2 and R^3 may be the same or different and each represents a monovalent organic group or
20 a monovalent inorganic group such as a hydrogen atom or a halogen atom). The present invention comprises introducing an alkenyl group to the terminus by reacting the terminal site of the polymer formed by polymerization reaction of a vinyl monomer.
[0015]

25 Therefore, the site represented by $-CH_2(R^2)(R^3)-$ in the above general formula 2 is derived from a vinyl monomer. Thus, R^2 and R^3 can be said as "a group bound to a vinyl group of a vinyl monomer".

As the polymerization which comprises using a chain
30 transfer agent for producing the polymer containing the general formula 2 at a terminus, there may be mentioned a polymerization comprising using a halide as a chain transfer agent (telogen). As the halide, carbon tetrachloride, carbon tetrabromide, methylene chloride, methylene bromide or the like may be used.
35 However, by the method comprising using a chain transfer agent,

it is difficult in principle to synthesize a block copolymer by addition of a monomer. Thus, when using this polymerization method, it is required a method comprising carrying out living radical polymerization by using a product of this

5 polymerization as an initiator.

<Living radical polymerization>

Living radical polymerization is radical polymerization in which the activity of the polymerization terminus is maintained without being loosed. In its narrow sense, the term
10 "living polymerization" means that polymerization in which a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which terminally inactivated molecules and terminally activated ones are in equilibrium. The latter
15 definition is to be applied to the present invention. Living radical polymerization has recently been aggressively investigated by a number of groups. As examples, there may be mentioned, among others, the method which uses a chain transfer agent such as polysulfide, the method which uses cobalt
20 porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an organic halide, for instance,
25 is used as an initiator and a transition metal complex as a catalyst. In the present invention, it is not particularly restricted as for which method is to be used, but atom transfer radical polymerization is preferred in view of easy controllability. In atom transfer radical polymerization,
30 polymerization is carried out by using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical
35 Society, 1995, vol. 117, page 5614; Macromolecules, 1995, vol.

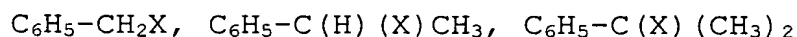
28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721). By these methods, polymerization proceeds as living polymerization and give polymers narrow in molecular weight distribution (Mw/Mn being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization generally having a very high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other.

[0016]

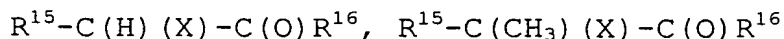
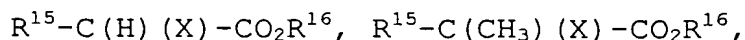
Since the living radical polymerization including atom transfer radical polymerization comprises such properties, a block copolymer can be produced by adding a monomer constituting the second block after polymerization of the first polymer block. Furthermore, since the terminal functional group can be controlled, it is also possible to produce the block copolymer (I) by coupling the polymer blocks.

<Polymerization initiator of atom transfer radical polymerization>

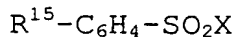
The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:



(in the above chemical formulas, C_6H_5 is a phenyl group and X is chlorine, bromine or iodine);



(in which R^{15} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and R^{16} represents a monovalent organic group having 1 to 20 carbon atoms); and



(in which R^{15} is a hydrogen atom or an alkyl group having 1 to

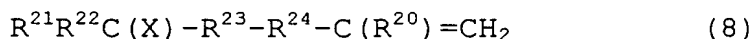
20 carbon atoms, an aryl group having 6 to 20 carbon atoms or aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

[0017]

5 Furthermore, when an organic halide or sulfonyl halide having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned
10 alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among others. By introducing an alkenyl group to the polymer produced from an initiator containing such functional group by various methods described later to produce the block copolymer (I), and adding the polymer to the living cationic polymerization system,
15 a block copolymer containing various functional group at its terminus can be easily obtained.

[0018]

When an alkenyl-containing initiator is used, the block copolymer (I) containing an alkenyl group at its terminus can
20 be easily obtained. The alkenyl-containing organic halide is not restricted but may be one having the structure shown by the general formula 8:



(wherein R^{20} is a hydrogen atom or a methyl group, R^{21} and R^{22}
25 each is a hydrogen atom or a monovalent alkyl having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and R^{21} and R^{22} may be bound to each other at respective other termini, R^{23} is $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group, R^{24} is a direct
30 bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is chlorine, bromine or iodine).

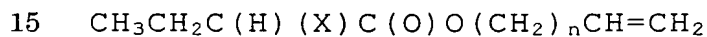
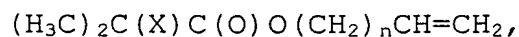
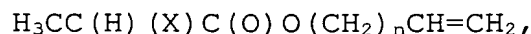
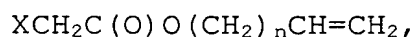
In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization
35 is started after the carbon-halogen bond is activated.

[0019]

As specific examples of the substituents R^{21} and R^{22} , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc. R^{21} and R^{22} may be bound to each other at respective other termini to form a cyclic skeleton. In such case, $-R^{21}-R^{22}-$ may be, for example, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ and the like.

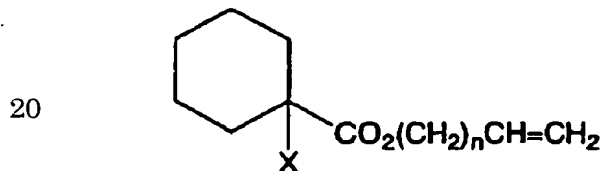
[0020]

As specific examples of the alkenyl-containing organic halide represented by the general formula 8, there may be mentioned the following:



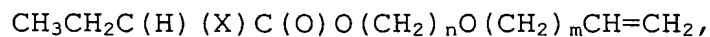
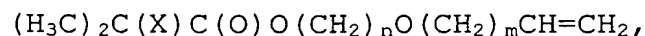
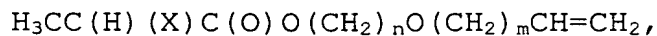
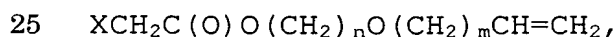
[0021]

[Chemical 3]



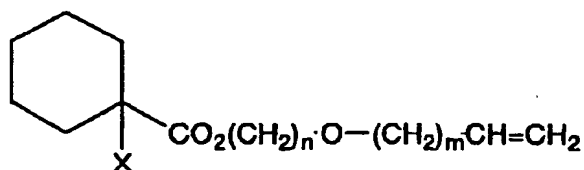
[0022]

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);



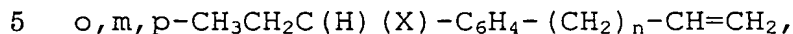
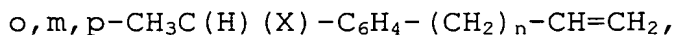
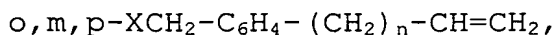
[0023]

30 [Chemical 4]

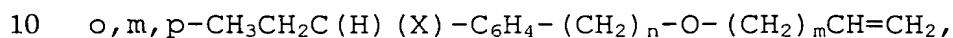
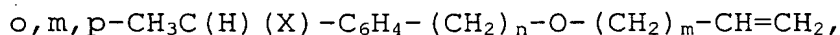
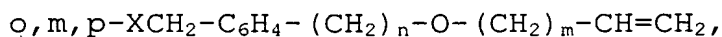


35 [0024]

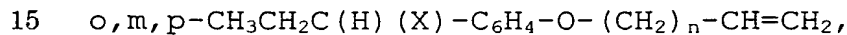
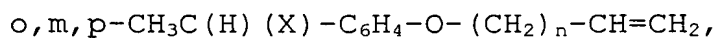
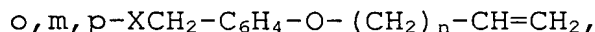
(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);



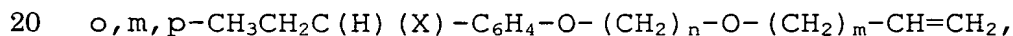
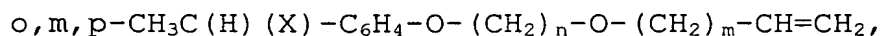
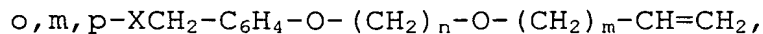
(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);



(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

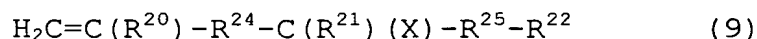


(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);



(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general
25 formula 9:



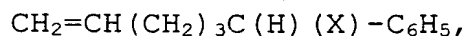
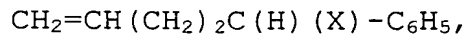
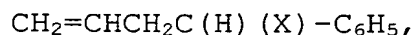
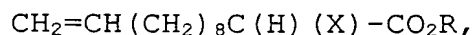
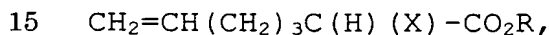
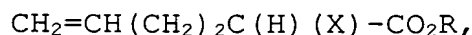
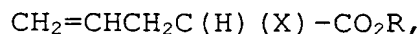
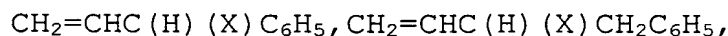
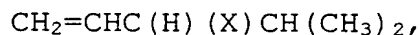
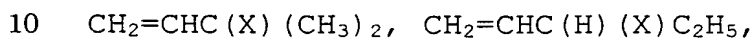
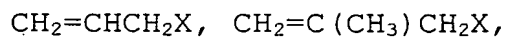
(wherein R^{20} , R^{21} , R^{22} , R^{24} and X are defined above and R^{25} is a direct bond, $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group).

30 R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the
35 neighboring vinyl group, so that it is not always necessary for

R^{25} to be a $C(O)O$ group or a phenylene group, for instance, but it may be a direct bond. When R^{24} is not a direct bond, R^{25} is preferably a $C(O)O$ group, $C(O)$ group or phenylene group so that the carbon-halogen bond may be activated.

5 [0025]

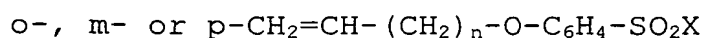
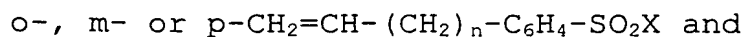
As a specific example of compounds represented by the general formula 9, there can be mentioned,



20 (in the above formulas, X is chlorine, bromine or iodine, and R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms). Among these, allyl chloride and allyl bromide are preferred from cost and availability viewpoint.

25 [0026]

Specific examples of the alkenyl-containing sulfonyl halide are as follows:



30 (wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20), among others.

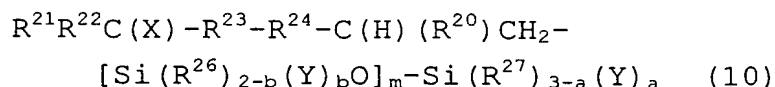
[0027]

When an alkenyl-containing initiator is used, care should be taken since there is a possibility that olefin of the
35 initiator may also react with the polymerization terminus.

Additionally, a polymer produced by using the alkenyl-containing initiator by itself becomes the block copolymer (I), but also has a growing terminus. The growing terminus may become not only a growing terminus of radical polymerization, but also an initiator of living cationic polymerization in which the block copolymer (I) is added. In this case, there may occur undesirable polymerization reaction other than the bond of the polymers, which the present invention intends to. For avoiding this reaction, the growing terminus (in many cases, a halogen group) may be removed by an alkaline treatment, and the like.

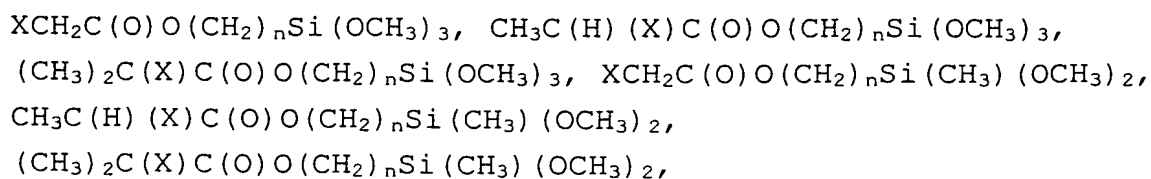
[0028]

The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, those having a structure shown by the general formula 10:

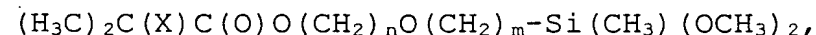
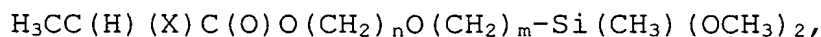
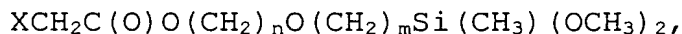
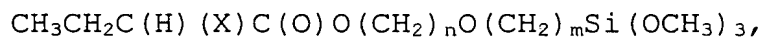
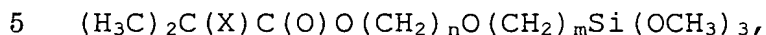
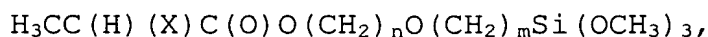
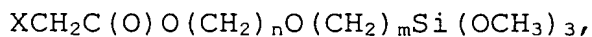


(wherein R^{20} , R^{21} , R^{22} , R^{23} , R^{24} and X are as defined above, R^{26} and R^{27} each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented by $(R')_3SiO-$ (in which R' is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R^{26} and/or R^{27} groups, they may be the same or different, Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different, a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation $a + mb \geq 1$ should be satisfied.

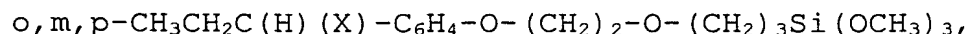
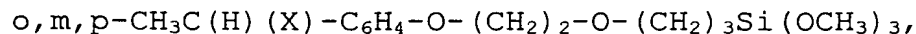
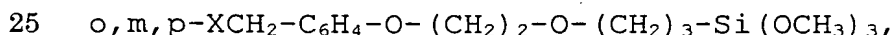
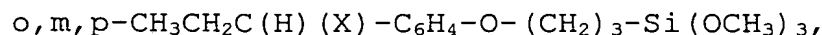
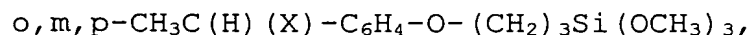
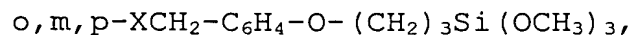
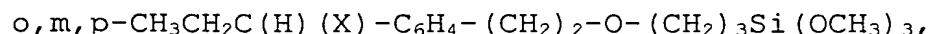
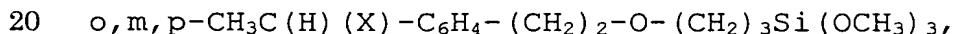
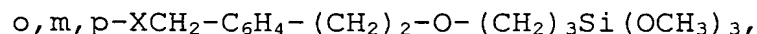
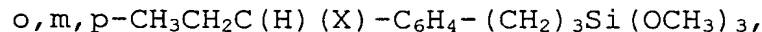
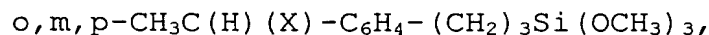
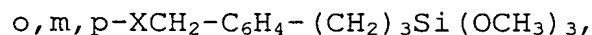
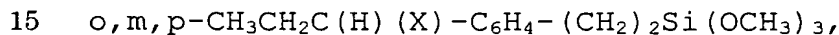
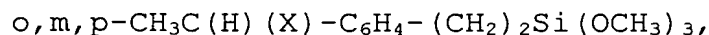
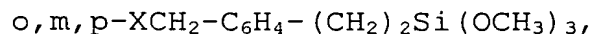
As a specific example of compounds represented by the general formula 10, there can be mentioned,



(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20),

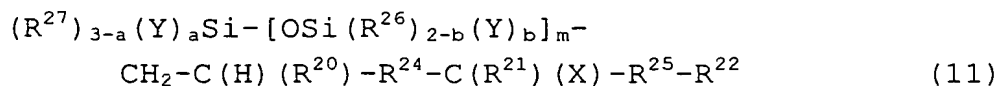


(wherein, in each formula, X is chlorine, bromine or iodine, n is an integer of 0 to 20, and m is an integer of 0 to 20),



(wherein, in each formula, X is chlorine, bromine or iodine).

As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 11:



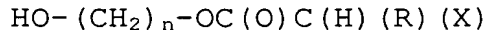
(wherein R^{20} , R^{21} , R^{22} , R^{24} , R^{25} , R^{26} , R^{27} , a, b, m, X and Y are as defined above).

As a specific example of such compounds, there can be mentioned;

$(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}_6\text{H}_5$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}_6\text{H}_5$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 5 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 10 (wherein, in each formula, X is chlorine, bromine or iodine,
 R is an alkyl group having 1 to 20 carbon atoms, an aryl group
 having 6 to 20 carbon atoms, or an aralkyl group having 7 to
 20 carbon atoms.), and the like.

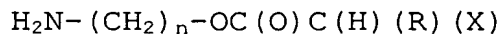
[0029]

15 The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



(wherein X is chlorine, bromine or iodine, R is a hydrogen atom
 20 or an alkyl group having 1 to 20 carbon atoms, an aryl group
 having 6 to 20 carbon atoms, or an aralkyl group having 7 to
 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide
 is not particularly restricted but includes compounds
 25 represented by the following formula:

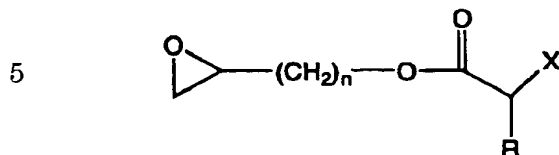


(wherein X is chlorine, bromine or iodine, R is a hydrogen atom
 or an alkyl group having 1 to 20 carbon atoms, an aryl having
 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon
 30 atoms and n is an integer of 1 to 20).

The above-mentioned epoxy-containing organic halide or
 sulfonyl halide is not particularly restricted but includes
 compounds represented by the following formula:

[0030]

[Chemical 5]



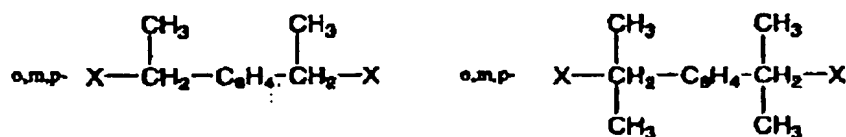
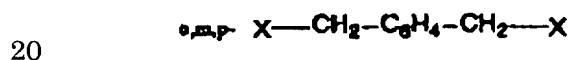
[0031]

(wherein X is chlorine, bromine or iodine, R is a hydrogen atom
 10 or an alkyl group having 1 to 20 carbon atoms, an aryl group
 having 6 to 20 carbon atoms, or an aralkyl group having 7 to
 20 carbon atoms and n is an integer of 1 to 20).

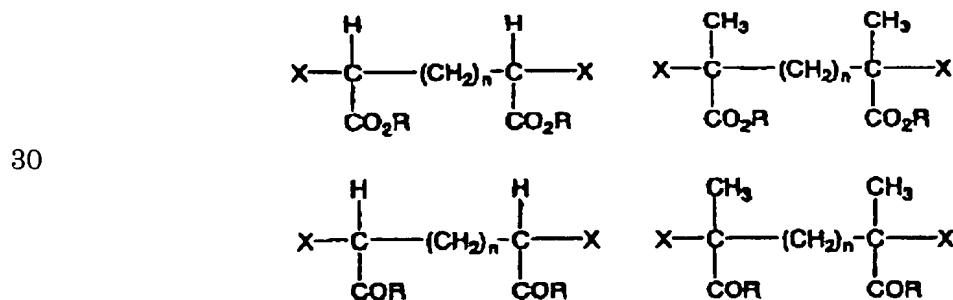
For obtaining polymers having two or more terminal
 structures represented by the general formula 2 within each
 15 molecule, an organic halide or sulfonyl halide having two or
 more initiation sites is used. Specific examples are:

[0032]

[Chemical 6]

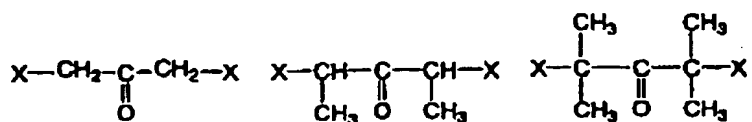


25 (in which C_6H_4 represents a phenylene group and X is chlorine,
 bromine or iodine);

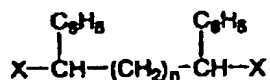


(in which R is an alkyl group having 1 to 20 carbon atoms, aryl
 35 or aralkyl group, n is an integer of 0 to 20 and X is chlorine,

bromine or iodine);



5

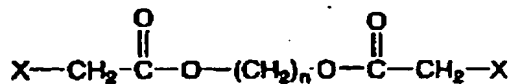


(in which X is chlorine, bromine or iodine and n is an integer of 0 to 20);

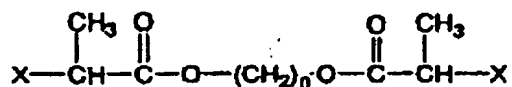
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[0033]

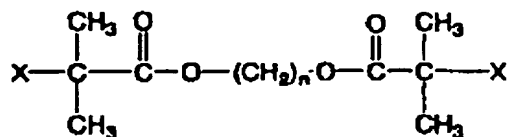
[Chemical 7]



15



20



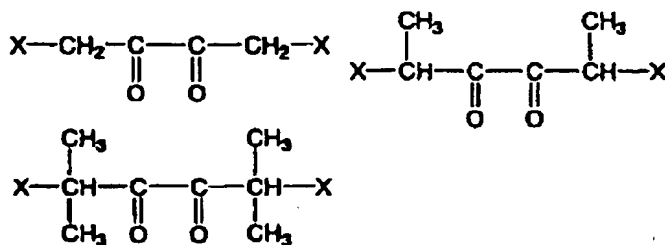
(in which n is an integer of 0 to 20 and X is chlorine, bromine or iodine);

25

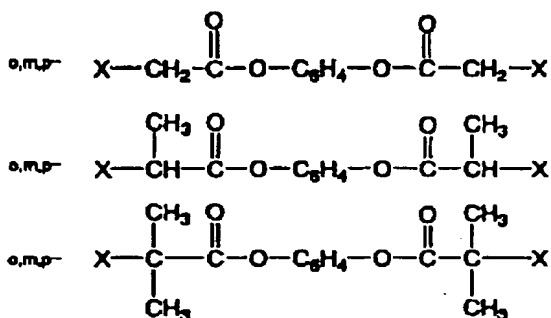
30

35

5



10



15



(in which X is chlorine, bromine or iodine), and the like.
[0034]

<Monomer>

20 The vinyl monomer to be used in controlled radical polymerization of the present invention is not particularly restricted and those mentioned above may be used.

<Catalyst>

25 The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably are complexes of monovalent copper, copper (valence: zero), divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred in view of cost and
30 reaction controllability. Specific examples of monovalent copper compounds are cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or
35 a derivative thereof or a polyamine such as

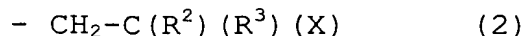
tetramethylethylenetriamine (TMEDA),
 pentamethyldiethylenetriamine or hexamethyl
 (2-aminoethyl)amine, is added to enhance the catalytic activity.
 A tris(triphenylphosphine) complex of divalent ruthenium
 5 chloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is also suited for use as a catalyst.
 When a ruthenium compound is used as a catalyst, an aluminum
 alkoxide is added as an activator. Furthermore, a
 bis(triphenylphosphine) complex of divalent iron ($\text{FeCl}_2(\text{PPh}_3)_2$),
 a bis(triphenylphosphine) complex of divalent nickel
 10 ($\text{NiCl}_2(\text{PPh}_3)_2$) and a bis(tributylphosphine) complex of divalent
 nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are also suited as catalysts.

<Solvent and temperature>

The above-mentioned atom transfer radical polymerization
 can be carried out in the absence or presence of various solvents.
 15 As the solvent, there may be mentioned, among others,
 hydrocarbon solvents such as benzene and toluene; ether
 solvents such as diethyl ether and tetrahydrofuran; halogenated
 hydrocarbon solvents such as methylene chloride and chloroform;
 ketone solvents such as acetone, methyl ethyl ketone and methyl
 20 isobutyl ketone; alcohol solvents such as methanol, ethanol,
 propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol;
 nitrile solvents such as acetonitrile, propionitrile and
 benzonitrile; ester solvents such as ethyl acetate and butyl
 acetate; and carbonate solvents such as ethylene carbonate and
 25 propylene carbonate. These may be used singly or two or more
 of them may be used in admixture. The above polymerization can
 be conducted within the temperature range of room temperature
 to 200°C, preferably 50°C to 150°C.

<Terminus conversion method>

30 The block copolymer (I) containing an alkenyl group at
 its terminus can be produced also by converting a halogen group
 of the thus obtained vinyl polymer having the terminal structure
 represented by the general formula 2:



35 (wherein R^2 and R^3 may be the same or different and each

represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.

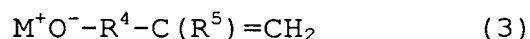
[0035]

5 The converting method is not particularly restricted, but there may be mentioned the following method.

<Oxy anion substitution>

The block copolymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula

10 3:

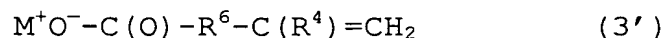


(wherein R^4 represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R^5 represents hydrogen, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M^+ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula 2.

20 In the following, the substitution method using an alkenyl-containing oxy anion is described in detail.

[0036]

In the general formula 3, which represents the alkenyl-containing oxy anion, R^4 and R^5 are the same substituent as defined above. As specific examples of these, all of those mentioned above may be used. Particularly, when R^4 is represented by $-C(O)-R^6-$, the above general formula 3 is represented by the general formula 3'.



30 In the above general formula 3, M^+ is a counter cation of an oxy anion, and represents an alkali metal ion or quaternary ammonium ion. As the above alkali metal ion, there may be mentioned lithium ion, sodium ion and potassium ion and, sodium ion or potassium ion is preferable. As the quaternary ammonium ion, there may be mentioned tetramethylammonium ion, 35 tetraethylammonium ion, trimethylbenzylammonium ion,

trimethyldodecylammonium ion and tetrabutylammonium ion, dimethyl piperidinium ion, among others.

[0037]

As example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may be mentioned the following:

$H_2C=CH-CH_2-OH$, $H_2C=CH-CH(CH_3)-OH$, $H_2C=C(CH_3)-CH_2-OH$,
 $H_2C=CH-(CH_2)_n-OH$ (n represents an integer 2 to 20),
 $H_2C=CH-CH_2-O-(CH_2)_2-OH$, $H_2C=CH-C(O)O-(CH_2)_2-OH$,
 10 $H_2C=C(CH_3)-C(O)O-(CH_2)_2-OH$, $o-, m-, p-H_2C=CH-C_6H_4-OH$,
 $o-, m-, p-H_2C=CH-CH_2-C_6H_4-OH$,
 $o-, m-, p-H_2C=CH-CH_2-O-C_6H_4-OH$,
 $o-, m-, p-H_2C=CH-C_6H_4-CH_2-OH$, $o-, m-, p-H_2C=CH-CH_2-C_6H_4-CH_2-OH$,
 $o-, m-, p-H_2C=CH-CH_2-O-C_6H_4-CH_2-OH$ and the like.

15 [0038]

Furthermore, as example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may also be mentioned the following:

$H_2C=CH-C(O)-OH$, $H_2C=C(CH_3)-C(O)-OH$, $H_2C=CH-CH_2-C(O)-OH$,
 20 $H_2C=CH-(CH_2)_n-C(O)-OH$ (n represents an integer 2 to 20),
 $H_2C=CH-(CH_2)_n-OC(O)-(CH_2)_m-C(O)-OH$ (m and n are the same or different, each represents an integer of 0 to 19),
 $o-, m-, p-H_2C=CH-C_6H_4-C(O)-OH$, $o-, m-, p-H_2C=CH-CH_2-C_6H_4-C(O)-OH$,
 $o-, m-, p-H_2C=CH-CH_2-O-C_6H_4-C(O)-OH$,
 25 $o-, m-, p-H_2C=CH-(CH_2)_n-OC(O)-C_6H_4-C(O)-OH$ (n represents an integer 0 to 13) and the like. These are the compounds which may also be represented by the above general formula 3'.

[0039]

The alkenyl-containing oxy anion represented by the general formula 3 may be prepared by reacting the above-mentioned precursor and a base. As the base, various ones may be used. Examples thereof include sodium methoxide, potassium methoxide, lithium methoxide, sodium ethoxide, potassium ethoxide, lithium ethoxide, sodium tert-butoxide, potassium tert-butoxide, sodium carbonate, potassium

carbonate, lithium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, sodium hydride, potassium hydride, methyllithium, ethyllithium, n-butyllithium, tert-butyllithium, lithium diisopropylamide, 5 lithium hexamethyldisilazide; alkylamines such as trimethylamine, triethylamine and tributylamine; polyamines such as tetramethylethylenediamine and pentamethyldiethylenetriamine; pyridine compounds such as pyridine and picoline; and so forth. The base is used in 0.5 10 to 5 equivalent amount, preferably 0.8 to 1.2 equivalent amount, relative to the precursor.

[0040]

As the solvent to be used in reacting the above precursor with the base, there may be mentioned, among others, hydrocarbon 15 solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, 20 propanol, isopropanol, n-butyl alcohol and t-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate solvents such as ethylene carbonate and propylene carbonate; and amide solvents such as 25 dimethylformamide and dimethylacetamide. These may be used singly or two or more of them may be used in admixture.

[0041]

Specific production method of the alkenyl-containing oxy anion represented by the general formula 3 is further described 30 in detail. For example, when o-, m- or p-H₂C=CH-CH₂-C₆H₄-OH is used as the precursor, a base, for example potassium tert-butoxide, is charged into a reaction vessel in an inert gas atmosphere, and is suspended and dispersed in a solvent such as dimethyl acetoamide. To this dispersion solution, the above 35 allyl phenol is added in equivalent molar amount, and the

mixture is subjected to reaction at room temperature to 70°C for 30 minutes to 1 hour, thereby an alkenyl-containing oxy anion in which potassium is substituted for an acidic proton can be obtained.

5 [0042]

The alkenyl-containing oxy anion in which M^+ is a quaternary ammonium ion can be obtained by directly reacting the above precursor with alkylamine or a pyridine compound. It can also be obtained by preparing one in which M^+ is a quaternary ammonium ion and reacting this with a quaternary ammonium halide. Examples of the quaternary ammonium halide are tetramethylammonium halides, tetraethylammonium halides, trimethylbenzylammonium halides, trimethyldodecylammonium halides and tetrabutylammonium halides, among others.

15 [0043]

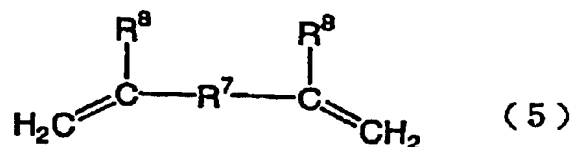
By reacting the alkenyl-containing oxy anion represented by the general formula 3 prepared by the above method with the vinyl polymer having the terminal structure represented by the general formula 2, the polymer (I) containing the group represented by the general formula 1 at the main chain terminus can be obtained. This reaction can be carried out in the fore-mentioned solvent at 0 to 150°C. The amount to be used of the alkenyl-containing oxy anion represented by the general formula 3 is 1 to 5 equivalent amount and preferably 1 to 1.2 equivalent amount relative to the terminal structure represented by the general formula 2.

<Unconjugated diene>

The block copolymer (I) having the structure represented by the general formula 1 at the terminus is also produced by adding a compound represented by the general formula 5:

30 [0044]

[Chemical 8]

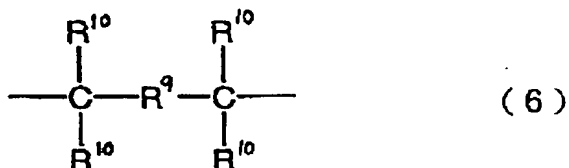


5 [0045]

{wherein R^7 represents an alkyl group containing 1 to 20 carbon atoms, or a group having a structure represented by the general formula 6:

[0046]

10 [Chemical 9]



15 [0047]

(wherein R^9 represents an oxygen atom, nitrogen atom or organic group containing 1 to 20 carbon atoms; R^{10} may be the same or different and represents a hydrogen atom or a methyl group) and R^8 represents a hydrogen atom or a methyl group} during or after completion of polymerization by various living radical polymerizations.

In the general formula 5, as specific examples of R^7 , there may be mentioned;

- 25 $-(\text{CH}_2)_n-$ (n is an integer of 1 to 20), $-\text{CH}(\text{CH}_3)-$, $-\text{CH}(\text{CH}_2\text{CH}_3)-$,
 $-\text{C}(\text{CH}_3)_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-$, $-\text{C}(\text{CH}_2\text{CH}_3)_2-$, $-\text{CH}_2\text{CH}(\text{CH}_3)-$,
 $-(\text{CH}_2)_n-\text{O}-\text{CH}_2-$ (n is an integer of 1 to 19), $-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2-$,
 $-\text{CH}(\text{CH}_2\text{CH}_3)-\text{O}-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-\text{O}-\text{CH}_2-$, $-\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-\text{O}-\text{CH}_2-$,
 $-\text{C}(\text{CH}_2\text{CH}_3)_2-\text{O}-\text{CH}_2-$, $-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-$
 (m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
 30 $-(\text{CH}_2)_n-\text{C}(\text{O})\text{O}-(\text{CH}_2)_m-$
 (m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
 $-(\text{CH}_2)_n-\text{OC}(\text{O})-(\text{CH}_2)_m-\text{C}(\text{O})\text{O}-(\text{CH}_2)_1-$
 (l is an integers of 0 to 18, m and n are integers of 1 to 17,
 however, $2 \leq l + m + n \leq 20$),
 35 $-(\text{CH}_2)_n-\text{o}-$, m- or p- C_6H_4- , $-(\text{CH}_2)_n-\text{o}-$, m-, p- $\text{C}_6\text{H}_4-(\text{CH}_2)_m-$

(m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 $1 \leq m + n \leq 14$),

$-(CH_2)_n-o-$, m- or p- $C_6H_4-O-(CH_2)_m-$

(m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 5 $1 \leq m + n \leq 14$),

$-(CH_2)_n-o-$, m- or p- $C_6H_4-O-CH(CH_3)-$

(n is an integer of 1 to 12),

$-(CH_2)_n-o-$, m- or p- $C_6H_4-O-CH(CH_3)_2-$

(n is an integer of 1 to 11),

10 $-(CH_2)_n-o-$, m- or p- $C_6H_4-C(O)O-(CH_2)_m-$

(m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),

$-(CH_2)_n-OC(O)-o-$, m- or p- $C_6H_4-C(O)O-(CH_2)_m-$

(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),

$-(CH_2)_n-o-$, m- or p- $C_6H_4-OC(O)-(CH_2)_m-$,

15 (m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),

$-(CH_2)_n-C(O)O-o-$, m- or p- $C_6H_4-(CH_2)_m-$,

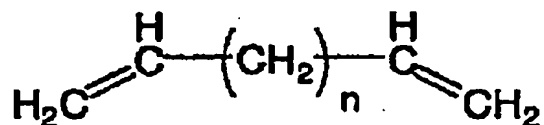
(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),
 and the like.

[0048]

20 R^8 is a hydrogen atom or a methyl group, but preferably
 a hydrogen atom. When R^7 is an alkyl group having 1 to 20 carbon
 atoms, its structure is not particularly restricted, but there
 may be mentioned the following.

[0049]

25 [Chemical 10]



30 [0050]

From the availability viewpoint of raw materials, n is
 preferably 2, 4 or 6.

A compound containing two alkenyl groups represented by
 the general formula 5 is preferably added in an excess amount
 35 during or at a terminal stage of living radical polymerization.

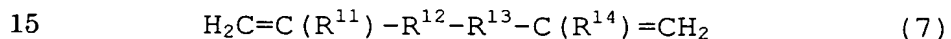
The terminal stage of polymerization is a point at which preferably not less than 80% and more preferably not less than 90% of monomers are reacted.

<Alkenyl-containing monomer>

5 The block copolymer (I) can also be produced by adding a compound having both an alkenyl group with high radical polymerizability and an alkenyl group with low radical polymerizability during or after completion of the living radical polymerization.

10 [0051]

The compound having both an alkenyl group with high radical polymerizability and an alkenyl group with low radical polymerizability is not particularly restricted, but there may be mentioned compounds represented by the general formula 7;



(wherein R^{11} and R^{14} represent hydrogen or methyl, R^{12} represents $-\text{C}(\text{O})\text{O}-$ (ester group) or ortho-, meta- or para-phenylene group and R^{13} represents a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally have one or
20 more ether bonds).

A polymer is produced by living radical polymerization, and further the above-mentioned compound having both a polymerizable alkenyl group and at least one alkenyl group other than that is reacted as the second monomer. In living radical
25 polymerization, the polymerization terminus has the polymerization activity, thus when a vinyl monomer is newly added, polymerization proceeds again. Therefore, when the vinyl monomer having both a polymerizable alkenyl group and at least one alkenyl group other than that is added, radical
30 addition reaction occur in the alkenyl group site with polymerization activity. Then, the other alkenyl group remains unreacted, so that an alkenyl-terminated polymer is obtained. Such monomer may be newly reacted by adding with a catalyst after completion of the polymerization and then
35 isolating the polymer, or may be reacted by adding during the

polymerization (in-situ). In the latter case, the higher the monomer conversion rate of the polymerization is, the more preferable it is. It is preferably not less than 80%. If it is not more than 80%, an alkenyl group distributes not in the molecular terminus but in the side chain, thereby mechanical property of the cured product is deteriorated.

[0051]

In this case, when such compound comprising both a polymerizable alkenyl group and at least one alkenyl group other than that is added in an equal amount to the number of the polymerization terminus (since it is living polymerization, almost equal to the number of initiation site of the initiator), principally, to all the terminus, one alkenyl group is to be introduced. However, for surely introducing an alkenyl group to the entire terminus, an excess amount, specifically 1 to 5 equivalent amount of the compound is preferably used. When more than 5 equivalent amount of the compound is used, an alkenyl group is introduced to a terminus of the polymer in high density, it is not preferable in view of cured product physical property.

[0053]

In the above general formula 7, one containing an ester group as R^{12} is a (meth)acrylate compound, and one containing a phenylene group as R^{12} is a styrenic compound. As R^{13} in the general formula 7, there may be mentioned alkylene groups such as methylene, ethylene and propylene; o-, m- or p-phenylene group; aralkyl groups such as benzyl; and alkylene groups containing an ether bond, such as $-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2-$ and $-\text{O}-\text{CH}_2-$.

[0054]

Among these, the following compounds are preferred because of their ready availability.

$\text{H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{CH}=\text{CH}_2$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{CH}=\text{CH}_2$,
(in each formula, n represents an integer of 0 to 20);

$\text{H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH}=\text{CH}_2$,

$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m\text{CH}=\text{CH}_2$,

(in each formula, n represents an integer of 0 to 20, and m

represents an integer 0 to 20);

o-, m-, p-divinylbenzene,

o-, m-, p-H₂C=CH-C₆H₄-CH₂CH=CH₂,

o-, m-, p-H₂C=CH-C₆H₄-CH₂-C(CH₃)=CH₂,

5 o-, m-, p-H₂C=CH-C₆H₄-CH₂CH₂CH=CH₂,

o-, m-, p-H₂C=CH-C₆H₄-OCH₂CH=CH₂,

o-, m-, p-H₂C=CH-C₆H₄-OCH₂-C(CH₃)=CH₂,

o-, m-, p-H₂C=CH-C₆H₄-OCH₂CH₂CH=CH₂,

o-, m-, p-H₂C=C(CH₃)-C₆H₄-C(CH₃)=CH₂,

10 o-, m-, p-H₂C=C(CH₃)-C₆H₄-CH₂CH=CH₂,

o-, m-, p-H₂C=C(CH₃)-C₆H₄-CH₂C(CH₃)=CH₂,

o-, m-, p-H₂C=C(CH₃)-C₆H₄-CH₂CH₂CH=CH₂,

o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂CH=CH₂,

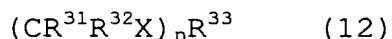
o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂-C(CH₃)=CH₂,

15 o-, m-, p-H₂C=C(CH₃)-C₆H₄-OCH₂CH₂CH=CH₂,

(in the above formulas, C₆H₄ denotes a phenylene group).

<Living cationic polymerization>

In the practice of the present invention, the living cationic polymerization for producing the desired block
20 copolymer by adding the above block copolymer (I) comprises polymerizing a cationically polymerizable monomer in the presence of a compound of the following general formula 12:



(wherein X is a substituent selected from a halogen atom, an
25 alkoxy group having 1 to 6 carbon atoms and an acyloxy group, R³¹ and R³² may be the same or different and each is a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, R³³ is a polyvalent aromatic or aliphatic hydrocarbon group and n is a natural number of 1 to 6).

30 <Monomer>

The monomer to be used for the living cationic polymerization according to the present invention is not particularly restricted but includes, for example, aliphatic
35 olefins, aromatic vinyls, dienes, vinyl ethers, silanes, vinylcarbazole, β-pinene, acenaphthylene and like monomers.

These are used singly or two or more of them are used combinedly. Specific examples of the monomer are shown below. From the viewpoint of physical properties of the product copolymers, isobutylene is preferred among others.

5 [0055]

As the aliphatic olefin monomers, there may be mentioned isobutylene, ethylene, propylene, 1-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, hexene, cyclohexene, 4-methyl-1-pentene, vinylcyclohexene, octene, norbornene and
10 the like.

As the aromatic vinyl monomers, there may be mentioned styrene, o-, m- or p-methylstyrene, α -methylstyrene, β -methylstyrene, 2,6-dimethylstyrene, 2,4-dimethylstyrene, α -methyl-o-methylstyrene,
15 α -methyl-m-methylstyrene, α -methyl-p-methylstyrene, β -methyl-o-methylstyrene, β -methyl-m-methylstyrene, β -methyl-p-methylstyrene, 2,4,6-trimethylstyrene, α -methyl-2,6-dimethylstyrene, α -methyl-2,4-dimethylstyrene, β -methyl-2,6-dimethylstyrene, β -methyl-2,4-dimethylstyrene,
20 o-, m- or p-chlorostyrene, 2,6-dichlorostyrene, 2,4-dichlorostyrene, α -chloro-o-chlorostyrene, α -chloro-m-chlorostyrene, α -chloro-p-chlorostyrene, β -chloro-o-chlorostyrene, β -chloro-m-chlorostyrene, β -chloro-p-chlorostyrene, 2,4,6-trichlorostyrene,
25 α -chloro-2,6-dichlorostyrene, α -chloro-2,4-dichlorostyrene, β -chloro-2,6-dichlorostyrene, β -chloro-2,4-dichlorostyrene, o-, m- or p-t-butylstyrene, o-, m- or p-methoxystyrene, o-, m- or p-chloromethylstyrene, o-, m- or p-bromomethylstyrene, silyl-substituted styrene
30 derivatives, indene, vinylnaphthalene and the like.

[0056]

As the diene monomers, there may be mentioned butadiene, isoprene, cyclopentadiene, cyclohexadiene, dicyclopentadiene, divinylbenzene, ethylenenorbornene and the like.
35 As the vinyl ether monomers, there may be mentioned methyl vinyl

ether, ethyl vinyl ether, (n-, iso)propyl vinyl ether, (n-, sec-, tert-, iso)butyl vinyl ether, methyl propenyl ether, ethyl propenyl ether and the like.

[0057]

5 As the silane compounds, there may be mentioned vinyltrichlorosilane, vinylmethyldichlorosilane, vinyldimethylchlorosilane, vinyldimethylmethoxysilane, vinyltrimethylsilane, divinyldichlorosilane, divinyldimethoxysilane, divinyldimethylsilane,
 10 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, trivinylmethylsilane, γ -methacryloyloxypropyltrimethoxysilane, γ -methacryloyloxypropylmethyldimethoxysilane and the like.

<Initiator>

15 The above-mentioned compound of the general formula 12 serves as an initiator and forms a carbon cation in the presence of a Lewis acid and the like, and carbon cation presumably serves as a site of initiation of cationic polymerization. As examples of the compound of the general formula 12 to be used in the
 20 present invention, there may be mentioned the following:

[0058]

(1-chloro-1-methylethyl)benzene [$C_6H_5C(CH_3)_2Cl$],
 1,4-bis(1-chloro-1-methylethyl)benzene
 [$1,4-Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl$],
 25 1,3-bis(1-chloro-1-methylethyl)benzene
 [$1,3-Cl(CH_3)_2CC_6H_4C(CH_3)_2Cl$],
 1,3,5-tris(1-chloro-1-methylethyl)benzene
 [$1,3,5-(ClC(CH_3)_2)_3C_6H_3$],
 1,3-bis(1-chloro-1-methylethyl)-(5-tert)-butylbenzene
 30 [$1,3-(C(CH_3)_2Cl)_2-5-(C(CH_3)_3)C_6H_3$]

Particularly preferred among them are bis(1-chloro-1-methylethyl)benzenes [$C_6H_4(C(CH_3)_2Cl)_2$]
 (bis(1-chloro-1-methylethyl)benzenes are also called bis(α -chloroisopropyl)benzenes, bis(2-chloro-2-propyl)benzenes or
 35 dicumyl chlorides). These are bifunctional initiators and,

when the polymerization is started with these, polymers having growing termini at both ends are obtained and these, upon reaction with the block copolymer (I), readily give block copolymers of the type ABCBA.

5 <Catalyst>

The polymerization for producing isobutylene-derived block copolymers may be carried out in the presence of a Lewis acid catalyst. Such Lewis acid may be any of those which can be used in cationic polymerization. Suited for use are, for example, metal halides such as TiCl_4 , TiBr_4 , BCl_3 , BF_3 , $\text{BF}_3 \cdot \text{OEt}_2$, SnCl_4 , SbCl_5 , SbF_5 , WCl_6 , TaCl_5 , VCl_5 , FeCl_3 , ZnBr_2 , AlCl_3 and AlBr_3 ; and organometal halides such as Et_2AlCl and EtAlCl_2 . Considering the catalytic activity and commercial availability, TiCl_4 , BCl_3 and SnCl_4 are preferred. The amount of the Lewis acid to be used is not particularly restricted but can be selected according to the polymerization characteristics or concentration of the monomer employed. Generally, the catalyst is used in an amount of 0.1 to 100 mole equivalents, preferably 1 to 60 mole equivalents, relative to the compound of the general formula 12.

20 <Electron-donating component >

The polymerization for producing isobutylene-derived block copolymers may also be carried out, when necessary, in the presence of an electron-donating component. Said electron-donating component is considered to have a stabilizing effect on growing carbon cations in cationic polymerization and, upon adding such electron donor, polymers having a controlled structure narrow in molecular weight distribution are formed. The electron-donating component which can be used is not particularly restricted but includes, among others, pyridines, amines, amides, sulfoxides, esters and metal compounds having an oxygen atom bound to the metal atom.

[0059]

The amount of use of each component can adequately be designed according to the characteristics of the desired

polymer. First, the molecular weight of the product polymer can be determined based on the mole equivalent relationship between the cationically polymerizable monomer other than the isobutylenic monomer and isobutylene and the compound of the general formula 12. Generally, designing is made so that the product block copolymer may have a number average molecular weight of about 20,000 to 500,000.

<Polymerization conditions>

The present invention can be carried out in a solvent, if necessary. Any solvent can be used without any particular limitation provided that it will not substantially inhibit the cationic polymerization. Typically, there may be mentioned halogenated hydrocarbons such as methyl chloride, dichloromethane, chloroform, ethyl chloride, dichloroethane, n-propyl chloride, n-butyl chloride and chlorobenzene; benzene and alkylbenzenes such as toluene, xylene, ethylbenzene, propylbenzene and butylbenzene; straight-chain aliphatic hydrocarbons such as ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane; branched aliphatic hydrocarbons such as 2-methylpropane, 2-methylbutane, 2,3,3-trimethylpentane and 2,2,5-trimethylhexane; alicyclic hydrocarbons such as cyclohexane, methylcyclohexane and ethylcyclohexane; paraffin oils purified from petroleum fractions by hydrogenation; and the like. Among these, toluene-containing mixed solvents are preferred in view of safety to the environment and polymerization physical properties. Primary and/or secondary monohalogenated hydrocarbons containing 3 to 8 carbon atoms are also preferably used. As specific examples of such that can be used are 1-chloropropane, 1-chloro-2-methylpropane, 1-chlorobutane, 1-chloro-2-methylbutane, 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylbutane, 1-chloro-3,3-dimethylbutane, 1-chloro-2,3-dimethylbutane, 1-chloropentane, 1-chloropentane, 1-chloro-2-methylpentane, 1-chloro-3-methylpentane, 1-chloro-4-methylpentane,

1-chlorohexane, 1-chloro-2-methylhexane,
 1-chloro-3-methylhexane, 1-chloro-4-methylhexane,
 1-chloro-5-methylhexane, 1-chloroheptane, 1-chlorooctane,
 2-chloropropane, 2-chlorobutane, 2-chloropentane,
 5 2-chloropentane, 2-chlorohexane, 2-chloroheptane,
 2-chlorooctane and chlorobenzene. These may be used singly or
 two or more of them may be used in combination. Among them,
 1-chlorobutane is preferred from the viewpoint of equilibrium
 among solubility of isobutylene-derived block copolymers, ease
 10 of decomposition for rendering the same nonhazardous, cost and
 other factors.

[0060]

These solvents are used singly or in combination
 considering the balance between the polymerization
 15 characteristics of the monomers constituting the block
 copolymer and the solubility of the product polymer, for
 instance.

The amount of solvent to be used is selected, considering
 the viscosity of the polymer solution to be obtained and the
 20 ease of removal of heat, so that the polymer concentration may
 be 1 to 50% by weight, preferably 5 to 35% by weight.

[0061]

In practicing the polymerization, the respective
 components are mixed up with cooling, for example at a
 25 temperature of -100°C to not higher than 0°C . A particularly
 preferred temperature range for attaining a balance between the
 cost of energy and the stability of polymerization is -30°C to
 -80°C .

<Addition of block copolymer (I)>

30 The time for adding the block copolymer (I) to the living
 cationic polymerization system is not particularly restricted
 but is preferably in the terminal stage of polymerization.
 According to the production method employed, the block
 copolymer (I) may have a cationically active terminal halogen
 35 group. For example, there can be mentioned the case with the

atom transfer radical polymerization using an allyl halide as an initiator to produce the block copolymer (I). In that case, it is possible that cationic polymerization starts from that site. Also in cases where such is to be avoided, the addition
5 should preferably be made at the final stage of polymerization where the monomer remains little.

[0062]

The amount of the block copolymer (I) to be added is not particularly restricted but is preferably such that the number
10 of growing termini in living cationic polymerization be equal to the number of the terminus represented by the general formula 1 in block copolymer (I).

The block copolymer (I) may be added as such or in the form of a solution in a solvent which will not adversely affect
15 the living cationic polymerization.

<Product>

The structure of the block copolymer produced is not particularly restricted, and is defined according to the structure of the block copolymer (I) to be added and the
20 structure of the polymer produced by living cationic polymerization. Among these, the polymer blocks A and B in the general formula 1 are preferably selected from among a styrenic polymer, (meth)acrylic polymer and acrylonitrile polymer. Moreover, it is preferable that the polymer block A is a styrenic
25 polymer and the polymer block B is an acrylic polymer; the polymer block A is a methacrylic polymer and the polymer block B is an acrylic polymer; and the polymer block A is a methacrylic polymer and the polymer block B is a styrenic polymer. The living cationic polymerization system to which the block
30 copolymer (I) is added is preferably a polyisobutylene polymerization system. Further preferably, the polymerization system is started from a difunctional initiator and the product becomes a polymer of the type ABCBA.

<Uses>

35 <Thermoplastic elastomer>

The block copolymer obtained by the production method of the present invention can be used in substantially the same fields of application as the existing styrenic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block copolymer with resins (with a plasticizer, a filler, a stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and exterior, electric and electronic fields, food wrapping films and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the block copolymer obtained by the production method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, compatibilizing agent, flattening agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.

[0063]

The thermoplastic resins which can be improved in shock resistance by addition of the block copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic

acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and the like. Said block copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0064]

As the method of adding the block copolymer of the present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0065]

Furthermore, in the resulting resin compositions, there may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether,

and antimony trioxide; pigments such as titanium oxide, zinc sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0066]

5 [Effect of the Invention]

By adding, according to the present invention, various alkenyl-terminated polymers to a polymerization system for living cationic polymerization, it is possible to obtain, with ease, block copolymers resulting from binding of these various
10 polymers to one another. Furthermore, by producing the polymer to be added by controlled radical polymerization, block copolymers well controlled in the molecular weight of the polymer block to be bound can be obtained. Since the species of the block and the molecular weight of the block copolymer
15 produced by the present patent can be easily controlled, it is easy to control the physical property.

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a block copolymer composed of any of various block copolymers and a cationic polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer having three or more polymer blocks can be produced easily by adding a block copolymer (I) containing an alkenyl group in at least one terminus to a living cationic polymerization system. Furthermore, said block copolymer (I) is produced by using controlled radical polymerization while easily being well controlled in the molecular weight. As the result, a block copolymer well controlled in the molecular weight of the polymer block to be bound can be obtained.

[Selective Figure] none